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## X.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

# CERTAIN BROMINE DERIVATIVES OF RESORCINE.

By C. Loring Jackson and F. L. Dunlap.

Presented February 14, 1894.

The research described in the following paper was suggested by the observation* that tribromnitroresorcine diethylether, when heated with a solution of sodic ethylate, lost two atoms of bromine, which were replaced by two of hydrogen, so that $C_6Br_3NO_2(OC_2H_5)_2$ was converted into $C_6BrH_2NO_2(OC_2H_5)_2$. Considering the easy removal of these two atoms of bromine, it seemed possible that the tribromresorcine diethylether, which differs from it only in the absence of the nitro group, might behave in a similar way. This expectation has not been fulfilled, as our experiments have shown that tribromresorcine diethylether does not give up bromine to sodic ethylate at the boiling point of alcohol, and that the dibrom ether is not attacked below 200°, and therefore is, if anything, more stable than the symmetrical tribrombenzol, which according to Blau† is slowly converted into dibromanisol at temperatures of 120° to 130°. The behavior of free tribromresorcine was next studied, and it was found that bromine could be removed with great ease, even water at its boiling point decomposing this substance, while solutions of sodic carbonate, or sodic hydrate, or sodic ethylate dissolved in alcohol acted even more readily. These results show that the ethoxyl groups do not loosen the attachment of the bromine atoms to the benzol ring, whereas the hydroxyl groups have as much of this loosening effect as do the nitro groups in tribromdinitrobenzol.

We have not succeeded in determining the nature of the organic compounds produced by removing bromine from tribromresorcine, as they were brown amorphous bodies, which could not be brought into a state of undoubted purity for analysis. From their properties, however, it can be inferred that they are substituted resorcine ethers formed by a reaction involving the hydroxyl groups of the tribromresorcine. Sodium malonic ester gave a similar unmanageable product with tribromresorcine, but in addition to this acetylentetracarboxylic ester was isolated. This substance could hardly be formed here otherwise than by the action of brommalonic ester on sodium malonic ester, and the brommalonic ester must have been formed by the replacement by hydrogen of one or more atoms of bromine in the tribromresorcine. It follows, therefore, that in this respect also the two hydroxyl radicals behave like the two nitro groups in tribromdinitrobenzol, in which a similar replacement of bromine by hydrogen has been observed when this substance is treated with sodium malonic ester.

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* These Proceedings, XXVII. 315.

† Monatsh. f. Chem., VII. 630.

The tribromresorcine diethylether melts at 68°–69°, and is formed by the action of an excess of bromine on the dibromresorcine diethylether, melting point 99°–100°. This latter substance is prepared by the addition of bromine to a solution of resorcine diethylether in glacial acetic acid. The tribrom product was shown to have the bromine atoms in the symmetrical position to each other by treatment with nitric acid, which converted it into the tribromnitroresorcine diethylether melting at 101°, which is made from symmetrical tribromtrinitrobenzol.* The action of nitric acid on dibromresorcine diethylether was entirely different, as the product was a new dinitroresorcine diethylether melting at 126°, formed by the replacement of the two atoms of bromine by two nitro groups. A similar replacement of bromine by nitro groups was observed when the tribromresorcine was treated with fuming nitric acid, the product being the bromdinitroresorcine described by Typke † and Fèvre. ‡ As this substance was obtained by the latter from dibromnitroresorcine, in this case also bromine was replaced by a nitro group, and several other cases are to be found in the chemical literature although they are far from common.

The most important point established by the observations given above is that in these cases hydroxyl or ethoxyl radicals have the same effect upon bromine which they have upon hydrogen attached to the benzol ring; for just as phenols are much more susceptible to the replacement of their hydrogen by halogens or nitro groups than the corresponding hydrocarbons, so the bromine can be replaced by other radicals, including the nitro group, much more easily in tribromresorcine than in tribrombenzol; while on the other hand the phenol ethers hold their hydrogen or bromine as firmly as the corresponding hydrocarbons. The one exception we have met with to this statement is the action of nitric acid upon dibromresorcine diethylether, in which the bromine is replaced by nitro groups, so that in this case the ether behaves like the free tribromresorcine rather than like the corresponding tribrom ether. This exception is the more remarkable, because we have found that toward other reagents, such as sodic ethylate, this dibrom ether shows the same great stability which characterizes the tribromresorcine diethylether.

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* These Proceedings, XXV. 183.

† Ber. d. ch. G., XVI. 555.

‡ Bull. Chem. Soc., XXXIX. 591.

As we could not remove the bromine from the tribromresorcine diethylether with sufficient ease, and the free tribromresorcine, although it gave up its bromine easily, gave unmanageable products since the hydroxyl groups took part in the reaction, we undertook the study of the tribromresorcine diacetate, which we hoped might give products that could be purified and analyzed; but these experiments did not lead to the desired result, as the acetate was converted into tribromresorcine by the reagents used, even boiling with water producing this effect to a slight extent, and consequently the products were those already mentioned as obtained from this substance. When treated with fuming nitric acid, the diacetate gives tribromnitroresorcine diacetate which melts at 161°.

The sodium salt of tribromresorcine was also studied. This was obtained in white crystals by precipitating an ethereal solution with alcoholic sodic ethylate, and seemed to contain two molecules of alcohol of crystallization. It was remarkable on account of its slight stability, as even *in vacuo* or in an atmosphere of hydrogen after standing for a short time it suddenly turned black, when there was a considerable evolution of heat and alcohol vapor was given off. The black residue gave up sodic bromide to water, and also a black soluble salt, while a red product was left behind. The black salt on the addition of acid gave a red precipitate similar to the product insoluble in water, but we were unable to bring either of these red amorphous substances into a condition undoubtedly fit for analysis; and although some analyses led to a very probable formula and reaction for the decomposition we can give no weight to these results, as we have no proof that the samples analyzed were homogeneous. There is no question that these substances are very similar to the products obtained from tribromresorcine and sodic ethylate or carbonate.

### *Dibromresorcine Diethylether*, $C_6H_2Br_2(OC_2H_5)_2$.

Resorcine diethylether, prepared by Pukall's method,* was dissolved in glacial acetic acid and bromine added to it until no more was taken up and a yellow color appeared in the solution. Crystals were soon seen to separate, and these were recrystallized from alcohol until they showed a constant melting point, when they were dried in a desiccator and analyzed with the following results: —

I. 0.2262 gram substance gave, according to the method of Carius, 0.2644 gram of argentic bromide.

II. 0.2272 gram substance gave 0.2628 gram of argentic bromide.

| | Calculated for $C_6H_2Br_2(OC_2H_5)_2$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Bromine | 49.38 | 49.74 | 49.22 |

*Properties.* — The dibromresorcine diethylether crystallizes in white silky felted long slender prisms terminated by one plane nearly at right angles to the sides; they melt at 99°–100°, and are slightly soluble in hot water; readily soluble in ether, benzol, and carbonic disulphide; very soluble in acetone and chloroform; also soluble in ligroin. Alcohol is the best solvent to use in purification.

In a sealed tube at 100° sodic ethylate does not react with dibromresorcine diethylether, nor was any action observed until the tube was heated to 200°, when, upon distillation of the product with steam, a few oil drops passed over. This experiment shows that the dibromresorcine diethylether is no more reactive than symmetrical tribrombenzol, if in fact as much so, since Blau has converted this latter substance, by heating it at 120°–130° with sodic methylate, into dibromphenol and its methylether.† As the interest in this work lay in the study of the effect of other radicals on the atoms of bromine rather than in the nature of the compounds formed, it was not thought worth while to spend the time necessary to prepare the product in quantity sufficient for its identification.

Dibromresorcine diethylether does not react with aniline in a sealed tube at temperatures ranging from 150° to 175°, and sodic phenolate at 230° also seems to have no effect upon it. It cannot therefore be called a very reactive substance.

### *Tribromresorcine Diethylether*, $C_6HBr_3(OC_2H_5)_2$.

The crystals of dibromresorcine diethylether were treated with an excess of bromine, and then heated upon a steam bath until the excess of bromine had evaporated. The reddish oil which resulted soon solidified and was recrystallized from alcohol until it showed the constant melting point of 68°–69°, when it was dried in a desiccator and analyzed.

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* Ber. d. ch. G., XX. 1141.

† Monatsh. f. Chem., VII. 630.

0.2222 gram of the substance gave, by the method of Carius, 0.3177 gram of argentic bromide.

| | Calculated for $C_6HBr_3(OC_2H_5)_2$. | Found. |
|---|---|---|
| Bromine | 59.55 | 59.70 |

This body crystallizes beautifully in long pearly fibres, often collected in bunches and sometimes branched, which melt at 68°–69° and are practically insoluble in cold water; very soluble in benzol and carbonic disulphide; readily soluble in ligroin and chloroform; quite soluble in acetone, but less soluble in ether. Alcohol is the best solvent for purification.

This tribrom ether reacts but very slightly with sodic ethylate at the boiling temperature of alcohol, and no more strikingly when boiled with sodic amylate. When boiled with aniline, the tribrom ether gave an amorphous black mass from which nothing definite could be obtained. Inasmuch as the sodic ethylate had so little action on this body, it was deemed unnecessary to carry this line of work farther, for the reasons given under the dibrom compound.

### *Constitution of Tribromresorcine Diethylether.*

Tribromresorcine diethylether dissolves readily in fuming nitric acid, giving the body $C_6Br_3NO_2(OC_2H_5)_2$, as was proved by its melting point, 100°–101°. As one of us and Warren [*] prepared this substance from symmetrical tribromtrinitrobenzol, this experiment proves the symmetrical position of the three bromine atoms in tribromresorcine diethylether.

### *Dinitroresorcine Diethylether,* $C_6H_2(NO_2)_2(OC_2H_5)_2$.

When dibromresorcine diethylether is treated with fuming nitric acid, the result is different from that obtained with the corresponding tribrom compound. To study this action, some of the dibrom ether was added to an excess of fuming nitric acid, when it immediately dissolved, after which it was treated with excess of water and the reddish oil which separated allowed to solidify. It was then recrystallized from alcohol till it showed the constant melting point of 126°, after which it was dried at 100° and analyzed.

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[*] These Proceedings, XXV. 183.

0.1313 gram of the substance gave 13.5 c. c. of moist nitrogen at a temperature of 26° and a pressure of 746.6 mm.

| | Calculated for $C_6(NO_2)_2H_2(OC_2H_5)_2$. | Found. |
|---|---|---|
| Nitrogen | 10.94 | 11.19 |

*Properties.* — The dinitroresorcine diethylether crystallizes from alcohol in radiated clusters of long white needles, or of smaller curved needles forming woolly masses. It is of a very faint yellow color and melts when pure at 126°. It is readily soluble in chloroform and acetone; slightly soluble in ligroin; soluble in benzol; tolerably soluble in carbonic disulphide; soluble also in ether. Alcohol is the best solvent for purification.

### *Tribromresorcine*, $C_6HBr_3(OH)_2$.

Tribromresorcine was prepared by the method of Benedikt,* as this yields better results than the treatment of resorcine dissolved in water with bromine, used by Hlasiwetz and Barth.† For this purpose the calculated amount of bromine is run into a solution of resorcine in cold glacial acetic acid. After the addition of the bromine this solution is somewhat warm, and upon cooling a finely crystallized product separates, which is best washed free from acetic acid by decantation. If more than the calculated amount of bromine is added, pentabromresorcine is formed in addition to the tribromresorcine. The yield by this method is slightly over 57 per cent of the theoretical.

A great many conflicting statements occur in the chemical literature regarding the melting point of tribromresorcine. Hlasiwetz and Barth, who discovered it, give no melting point. Typke,‡ in some work on tribromdioxyazobenzol, obtained a body with a constant melting point of 104°. The amount of this body that he had was too small for analysis, but a careful comparison of its properties, especially its melting point, its crystalline form, and its solubility, with that of tribromresorcine he had prepared himself, convinced him of the identity of the two substances.

Rudolph Benedikt § by the action of tin and hydrochloric acid upon Stenhouse's pentabromresorcine, obtained tribromresorcine which melted at 111°. He also gives analyses which agree very well indeed for the body in question.

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* Monatsh. f. Chem., IV. 227.

† Ann. Chem., CXXX. 357.

‡ Ber. d. ch. G., X. 1578.

§ Ibid., XI. 2168.

Von Pechmann,* three years later, obtained a body by the action of an excess of bromine upon benzolresorcinephthaleïn, which he called tribromresorcine on the ground of the melting point of 103°. He gives no analysis of this body, notwithstanding the fact that Benedikt had previously found its melting point to be 111°.

Beilstein in his "Handbuch" gives only Typke's melting point of 104°.

All of the tribromresorcine we have made use of in this research melted at 111°, the point given by Benedikt, and repeated recrystallization from water, which seems to be preferable to all other solvents, failed to raise its melting point higher.

According to Hlasiwetz and Barth,† tribromresorcine when recrystallized from water contains water of crystallization, which it loses at 100°. As the presence of water of crystallization might explain the differences in the melting points given by previous observers, we examined the tribromresorcine in this direction. Some of it was crystallized from hot water and dried in the air to a constant weight. This air-dried salt, which remained constant in a desiccator over calcic chloride, was heated to 100° for ten hours, when 0.2169 gram of the substance lost but 0.4 milligram in weight. Therefore tribromresorcine when recrystallized from water does not contain water of crystallization which it loses at 100°, as Hlasiwetz and Barth state.

In the recrystallization of the tribromresorcine from hot water, especially from boiling water, it was noticed that the crystals had a light pink color, so a study of the action of boiling water upon this body was taken up. One gram of the pure tribromresorcine was boiled in a 500 c. c. flask, fitted with an inverted condenser, with 250 c. c. of water. The greater part of the solid went into solution, and after the boiling had proceeded but a very short time the liquid became pink in color, which deepened into a dark red after the action had been carried on for twenty-four hours. The portion of the tribromresorcine which did not go into solution melted under the boiling water, its color also changing from a pink to a very dark red after the boiling had been continued for some time. At the end of twenty-four hours' boiling, we found that all of the tribromresorcine had not been changed into the red body, for on cooling crystals of a light pink color separated from the solution, which had the melting point of

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* Ber. d. ch. G., XIV. 1061.

† Ann. Chem., CXXX. 357.

111°. Even further boiling, it seemed, failed to complete the change. Upon the addition of argentic nitrate to this solution, a heavy precipitate of argentic bromide was obtained, showing that bromine had been removed from the tribromresorcine.

The red body which formed the organic product in the reaction was amorphous, and could not be recrystallized from any solvents we could find.

It was thought that possibly in a sealed tube the reaction would run much more smoothly, converting all the tribromresorcine into the amorphous red body. Consequently, quite a number of experiments were tried with varying amounts of the substance, heated from twelve to twenty-five hours at different temperatures, but without success. The tribromresorcine, it seems, is incapable of complete transformation into the red body at temperatures below 200°, while at 200° it is carbonized after heating for a short time. As the solubilities of the red body are practically the same as those of tribromresorcine, all methods for purification failed, and it could not be brought into a state fit for analysis. It is probable, however, that it contains more hydroxyl groups than the tribromresorcine, forming perhaps in the first place a substituted pyrogallol, (for in alkaline solutions the red body immediately blackens,) which is afterwards converted into more complex substances by reactions in which the hydroxyls bear a part.

Aniline or sodic alcoholates also acted easily with the tribromresorcine, but although much bromine was evidently removed in the form of hydrobromic acid or sodic bromide, in no case could any organic product be isolated in a state fit for analysis.

### *Sodium Salt of Tribromresorcine*, $C_6HBr_3(ONa)_2 . 2\,C_2H_5OH$.

This salt cannot be obtained from an aqueous solution, although it seemed to be formed, since upon treating tribromresorcine with a dilute solution of sodic carbonate carbonic dioxide was evolved, but the solution at once turned black and evidently underwent a deep-seated change. The following method for obtaining it was accordingly adopted. One gram of pure tribromresorcine was dissolved in absolute ether, and to this was added less than the calculated amount of sodium dissolved in absolute alcohol (the calculated amount of sodium is 0.13 gram). A precipitate immediately separated, consisting of short flat prisms having a silky lustre. These were filtered off and thoroughly washed with absolute ether. In the preparation of this body, the ether must be in large excess; if the reverse was true (that is, if the absolute alcohol were in excess) no precipitate was formed. The crystals were transferred, after washing with absolute ether, to a desiccator and allowed to dry in a stream of hydrogen. Some of the salt thus prepared was submitted to analysis. All the operations with this substance must be carried on as quickly as possible, since it has a strong tendency to decompose, forming a black mixture, and this change takes place even *in vacuo* or in an atmosphere of hydrogen, although not so quickly as when in contact with the air. Even during the weighing in a closed tube, the substance often decomposed, but the following analyses were made with the unchanged substance, although in all the analyses made the samples used were light brown in color, showing that slight decomposition had taken place.

I. 0.1357 gram of the salt gave 0.0396 gram sodic sulphate.
II. 0.1398 gram of the salt gave 0.0416 gram sodic sulphate.

| | Calculated for<br>$C_6HBr_3(ONa)_2 . 2 C_2H_5OH$ | Found.<br>I. | <br>II. |
|---|---|---|---|
| Sodium | 9.52 | 9.45 | 9.64 |

These results indicate that the salt contained two molecules of alcohol of crystallization, and that alcohol was present in the body was evident, for a great many times, in attempting to weigh it, the contents of the weighing tube would suddenly turn black, giving off heat, while a liquid collected in large drops on the sides of the tube which was recognized as alcohol.

*Properties.* — The sodium salt of tribromresorcine crystallizes in short flat prisms of a white color and a silky lustre. Its most striking property is its great instability, decomposing rapidly with the elimination of alcohol, the salt becoming black in color; when dissolved in water, the solution immediately turns black. A freshly prepared lot of this sodium salt was divided into two portions, one of which was put into a small tube through which a rapid stream of hydrogen was passing, the other was put into a test tube which was surrounded by a freezing mixture of salt and ice, the substance in the test tube being in contact with the air. It was found that the sodium salt in the stream of hydrogen (at ordinary temperature) blackened more rapidly than did the salt which was in the freezing mixture in contact with the air. This experiment proves that the salt is more stable in the cold than at ordinary temperatures, and also that the blackening is not due to oxidation. Since then we had proved that this behavior was not due to oxidation, it seemed possible that the black mixture obtained by drying at 100° might have the same percentage composition as the dried salt. Accordingly the amount of sodium was determined in a specimen of the salt which had been allowed to blacken and dried to a constant weight at 100°. The black body is slightly hygroscopic, so it must be weighed in a weighing tube.

0.2052 gram of the substance gave 0.0722 gram of sodic sulphate.

| | Calculated for $C_6HBr_3(ONa)_2$. | Found. |
|---|---|---|
| Sodium | 11.76 | 11.40 |

An attempt to determine the amount of alcohol present by heating some of the freshly prepared salt to 100° gave the following results: —

0.5944 gram of the substance lost at 100° 0.1068 gram in weight.

| | Calculated for $C_6Br_3H(ONa)_2 . 2\,C_2H_5OH$. | Found. |
|---|---|---|
| Alcohol | 19.05 | 17.97 |

This determination, although one per cent too low, is as near as we could expect it to come, inasmuch as it was impossible to obtain a sample for analysis which was perfectly white; but there is a more serious objection to this result and the determination of the sodium in the salt dried at 100°, as we have no proof that alcohol was the only substance volatilized during the decomposition and subsequent drying. In fact the determinations of the amount of sodic bromide contained in the dried mixture indicated that a certain quantity of hydrobromic acid might have been evolved. The only analyses of the salt, therefore, which are above suspicion, are those first given of the white undecomposed preparation.

The following experiments were tried to prove the nature of this decomposition of the salt. When the black decomposition product was dissolved in water, and dilute sulphuric acid added, a flocculent reddish brown precipitate was formed, which very much resembled ferric hydrate in appearance. The clear filtrate from this gave a very heavy precipitate of argentic bromide upon addition of argentic nitrate. This shows that the decomposition was produced by the elimination of a portion of the bromine from the ring. The amount of sodic bromide formed during the reaction was determined by treating the blackened salt with water of varying temperatures and for different lengths of time, and then the solutions were acidified with dilute sulphuric acid, the precipitate filtered off, and bromine determinations made in the clear filtrate. The results obtained were not constant, varying from 32.01 per cent to 37.90 per cent of bromine, and this variation may be explained by the supposition that a certain amount of hydrobromic acid escaped during the decomposition.

The study of the red flocculent precipitate obtained by the addition of sulphuric acid to an aqueous solution of the sodium salt of tribromresorcine has not led to any trustworthy results. Treatment with water and ether showed that it was not homogeneous, and the different fractions thus obtained could not be brought into a state fit for analysis, as no means of proving that they were pure could be found. Some of these analyses gave numbers agreeing fairly well with the very probable formula $[C_6H_2BrOH]_2O_2$; but for the reason just given it is impossible to accept this formula as established by them.

Tribromresorcine when treated with aqueous sodic carbonate dissolves with the evolution of carbonic dioxide, the solution immediately blackening, as has been stated already; upon acidification with dilute sulphuric acid a reddish brown flocculent precipitate was formed similar to that mentioned above, and the clear filtrate from this body gave a very heavy test for bromides. That in this case the blackening was not due to oxidation was shown by the fact that it took place in an atmosphere of hydrogen, even when the solution had been boiled to insure the absence of dissolved oxygen. Sodic or potassic hydrate has the same effect upon tribromresorcine as the carbonate. The red precipitate obtained upon acidifying has not yet been obtained in crystals, and when heated decomposed without melting, giving off hydrobromic acid. This body is doubtless the same as that obtained by the action of water on tribromresorcine, and also from the blackened sodium salt by acidifying its aqueous solution, as has been described above.

### *Action of Sodium Malonic Ester on Tribromresorcine.*

This reaction was taken up to see if another case of the peculiar substitution of bromine by hydrogen, already noticed by one of us,* could not be obtained. After a great many trials the best mode for studying the reaction was found to be as follows. Five grams of sodium were dissolved in 250–300 c. c. of absolute alcohol, and to this were added thirty-five grams of malonic ester. Twenty-five grams of tribromresorcine were then added, and this turned dark and afterward dissolved. After boiling the mixture for three hours in a flask fitted with an inverted condenser, the alcohol was distilled off and the contents of the flask were acidified with dilute sulphuric acid. A dark red oil separated, which was dissolved in ether, this solution then dried over calcic chloride, and the ether distilled off. Upon standing several days, the residual oil turned rather viscous, and crystals were seen permeating the mass. These crystals may be obtained by absorbing the oil with bibulous paper or by distilling *in vacuo*. By crystallization from dilute alcohol the constant melting point 76° was obtained, and as the crystals are white, contain no bromine, and their solubility, mode of crystallization, and shape correspond with those of acetylentetracarboxylic ester, there can be no doubt that they are this substance. This acetylentetracarboxylic ester could hardly have been formed otherwise than by the action of brommalonic ester on sodiummalonic ester, and the brommalonic ester it would seem must have been produced by the interchange of a bromine atom of the tribromresorcine with one of the atoms of hydrogen of the malonic ester. It follows from this reasoning, therefore, that we have here another case of the curious replacement of bromine by hydrogen, so often observed in this Laboratory, and that the two hydroxyl groups of the resorcine exercise the same action on one or more of the atoms of bromine as the two nitro groups in the tribromdinitrobenzol. The following fruitless attempt was made to isolate the other organic derivative formed. If the red oil absorbed by the bibulous paper, after the acetylentetracarboxylic ester has been separated as completely as possible, be treated with benzol, it is divided into a soluble and an insoluble portion. The insoluble portion, by precipitating an alcoholic solution of it with benzol, came down in a flocculent form, and when dry was light brick-red in color. It was evidently closely related to the substance obtained by the action of water or sodic carbonate on the tribromresorcine, and like that could not be purified.

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* These Proceedings, XXIV. 1, 256.

### *Action of Nitric Acid on Tribromresorcine.*

Fuming nitric acid reacts easily with tribromresorcine. The product was recrystallized from benzol and upon analysis gave the following results: —

0.2219 gram of the substance gave by the method of Carius 0.1479 gram of argentic bromide.

| | Calculated for $C_6HBr(NO_2)_2(OH)_2$. | Found. |
|---|---|---|
| Bromine | 28.67 | 28.37 |

This analysis and its melting point, 192°–193°, show it to be the body heretofore described by Typke * and Fèvre.†

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* Ber. d. ch. G., XVI. 555.

† Bull. Chem. Soc., XXXIX. 591.

We have found, in attempting to prepare the diacetate of dinitrobromresorcine, that dinitrobromresorcine would not react with acetyl chloride when heated with it at 100° for six hours in a sealed tube. Water does not react with dinitrobromresorcine in a sealed tube at temperatures varying from 100° to 150°. At temperatures between 150° and 190° the body is entirely decomposed, leaving a residue in the tube which seemed to be carbon, as it was insoluble in all solvents. It is strange that this substance should be less affected by water than the tribromresorcine, which is slowly acted on by water at its boiling point. The dinitrobromresorcine reacts with sodic ethylate, but, as in the case of the tribromresorcine, the resulting amorphous mass could not be purified or crystallized.

### *Behavior of Tribromresorcinediacetate.*

While the tribromresorcine itself reacts readily with boiling water and sodic ethylate, but gives unmanageable products, and the di- and tribromresorcine diethyl ethers do not act with these reagents, it was thought that possibly the diacetate of tribromresorcine might be better to work with than either of the ethers or the free phenol, because it holds an intermediate place between the acid tribromresorcine and its neutral ethers. Instead of using Claassen's method* of boiling pentabromresorcine with acetic anhydride, then with glacial acetic acid, and finally with water, the tribromresorcinediacetate was directly prepared from tribromresorcine by treating it in a sealed tube for four or five hours at 100° with either acetyl chloride or acetic anhydride, preferably the former. It is best to use a slight excess of acetyl chloride, and after the heating is finished to decompose the excess by means of water. The diacetate is easily recrystallized from alcohol, and was identified by its melting point, 108°.

After boiling tribromresorcinediacetate with water for twenty-four hours, the water was slightly pink in color, and gave a feeble test for bromides with argentic nitrate. This is due, no doubt, to the fact that water at 100° saponifies a small part of the diacetate, yielding tribromresorcine, which in its turn is acted upon by the boiling water, as before noted. In the hope of avoiding this saponification, a sealed tube containing the diacetate was heated over night at 157° with ordinary acetic acid, but the saponification was not prevented, for the result was the same as if the free tribromresorcine had been heated with water alone to that temperature. Sodic ethylate in alcoholic solution when warmed with tribromresorcinediacetate deposited a precipitate which when filtered off soon turned black. This body was undoubtedly the decomposition product of the sodium salt of tribromresorcine. On account of the readiness, therefore, with which the diacetate was saponified, it was not worth while to carry on this line of investigation further.

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* Ber. d. ch. G., XI. 1439.

### *Tribromnitroresorcinediacetate,* $C_6(NO_2)Br_3(OC_2H_3O)_2$.

The diacetate of tribromresorcine when added to an excess of fuming nitric acid immediately dissolved, and after standing several minutes the solution became very warm and began to boil, the body in solution becoming completely oxidized; but if just before the oxidation took place, when the solution was already hot, it was poured into an excess of water, the resulting yellowish oil soon solidified. The substance was purified by crystallization from alcohol until it showed the constant melting point of 161°, when it was dried at 100° and analyzed with the following results: —

0.1752 gram of the substance gave, by the method of Carius, 0.2086 gram of argentic bromide.

| | Calculated for $C_6NO_2Br_3(OC_2H_3O)_2$. | Found. |
|---|---|---|
| Bromine | 50.42 | 50.69 |

The diacetate therefore behaves toward nitric acid like the tribromether rather than like the tribromphenol itself, for in the latter and in the dibromether atoms of bromine are replaced by nitro groups, as already described earlier in this paper.

*Properties.* — The tribromnitroresorcinediacetate forms good-sized prisms terminated by two planes at an obtuse angle to each other; it is very pale yellow, almost white, and melts at 161°. It dissolves slowly in ligroin, is readily soluble in chloroform, benzol, and ether, quite soluble in acetone, and tolerably soluble in carbonic disulphide.

In order to establish if possible the position of the three bromine atoms in tribromresorcine, attempts were made to saponify the tribromresorcinediethylether, which has the three bromine atoms arranged symmetrically. When saponified in a sealed tube with aqueous hydrochloric acid, however, the product was a red body similar to that formed by the action of water on tribromresorcine. Accordingly, in hopes of a better result, dry hydrochloric acid gas was passed for one hour over tribromresorcinediethylether heated in an oil bath to 200°, but no saponification took place.